Photocatalytic ozonation: Maximization of the reaction rate and control of undesired by-products

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ABSTRACT

In the so-called photocatalytic ozonation (PO) synergistic effects between photocatalysis and ozonation enhance the rate of oxidation of organic compounds, therefore this integrated process is very promising for use in water treatment. In the present work, it is demonstrated that the improvement that can be obtained by the integrated process in comparison with the uncoupled processes depends on the relative weight between photocatalysis and ozonation. In this respect, it has been found that a relatively low rate of photocatalysis (0.3 times the rate of ozonation) is sufficient to get the highest synergy and to maximize the performances in the oxidation of formate, the adopted model organic compound. The benefits of the coupling of photocatalysis to ozonation are not limited to the increase of the oxidation rate, but include also the control of the ozonation by-product of main concern (bromate). The effect of the pH, of the presence of oxidizable organic compounds, of the presence of nitrogen on the formation or on the reduction of bromate are experimentally studied and discussed. The obtained results have relevance for the practical applications of PO, since on these bases it is possible to identify proper operating conditions.

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1. Introduction

Interest on advanced oxidation processes (AOPs) for water purification and recovery has significantly increased in the latest years. The main reason for this growing interest is the capability of AOPs to destroy recalcitrant and persistent toxic organic compounds [1–3], such as the pollutants of emerging concern [4], whose presence even at low concentration can be hazardous for human health and is not compatible with many utilizations. Ozonation (OZ) and particularly photocatalysis (PC) produce hydroxyl radicals, the strong oxidizing agent that characterizes AOPs, so they are capable of degrading organics possibly up to their complete mineralization.

However, despite the "green" features of photocatalysis [5,6], in particular if solar radiation is utilized for its activation, and the numerous and promising laboratory results [7], industrial applications of photocatalysis for water treatment are still very scarce [8]. Actually, photocatalysis is hampered by the slow kinetics, which is a consequence also of the low quantum yield [7]. Therefore, a

substantial enhancement of the rate is needed for future practical applications [8].

On the other hand, even the more established process of ozonation, which is currently used for disinfection and purification purposes in aquaculture [9,10] and in waste and drinking water treatment [11,12] is not problem-free. Actually, ozonation is negatively affected by the possible formation of undesired disinfection by-products (DBPs), such as bromate, which is a product of bromide oxidation [13,14] and is suspected to be carcinogenic.

Photocatalytic ozonation (PO), that is photocatalysis coupled with ozonation, can be a viable solution of the aforementioned problems. In fact, a synergistic effect substantially improves the oxidation rate in comparison with the rates obtained with the two processes acting in sequence [15–17] and photocatalysis may control the formation or the accumulation of bromate [18]. However, even if the synergetic effect in PO is well established and the capability of controlling the presence of bromate ions has been recently demonstrated [18], the identification of the more favourable operating conditions is still incomplete and needs further investigation.

Therefore, the aims of the present work are (i) to show that the synergy between the two processes can be maximized by tuning the relative weight between photocatalysis and ozonation, (ii) to identify the conditions (pH, presence of organic compounds, presence of oxygen, presence of nitrogen) that favour or limit the

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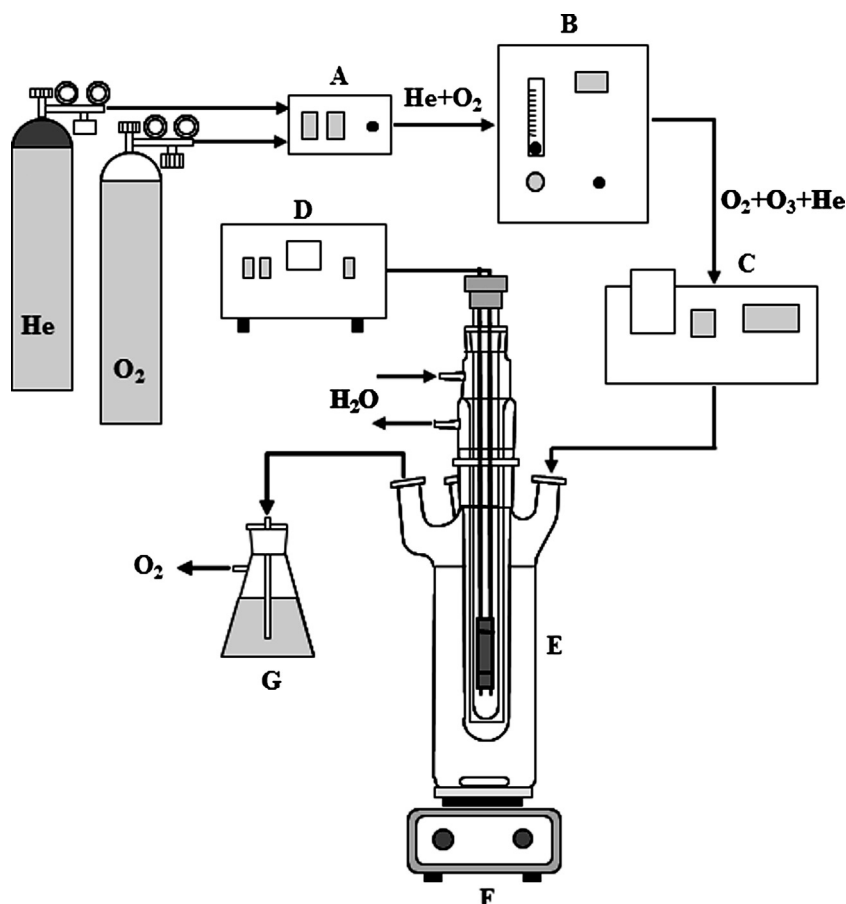leonardo.palmisano@unipa.it (L. Palmisano).

Fig. 1. Scheme of the experimental system. Mass controller (A); ozonator (B); UV–vis spectrophotometer (C); ballast of the lamp (D); reactor (E); magnetic stirrer (F); ozone trap (G).

formation of bromate, and (iii) to establish the operating conditions that improve the removal of bromate, in the case it is produced.

2. Experimental

The experimental set up is almost the same utilized in a previous study [18]. A description containing the essential information is reported below, but additional details can be found in [18].

The scheme of the experimental system is shown in Fig. 1. An annular slurry batch reactor (volume $500\,cm^3$) was utilized for all the OZ, PC and PO experiments. The collection of the samples of the reacting solution and the measurements of the pH took place at regular time intervals. The lamp, which is positioned on the axis of the reactor, emits a narrow spectrum of UVA radiation with a maximum at 365 nm. Borosilicate glass for the walls of the reactor minimizes the absorption of this radiation.

Ozone was produced by a corona discharge ozonator (Microlab) which was fed with $900\,cm^3\,min^{-1}$ of pure oxygen or alternatively with a He–O_2 mixture (80% He, 20% O_2). The resulting ozone concentrations are 4.9×10^{-4} M with pure oxygen and 0.55×10^{-4} M with the He–O_2 mixture. According to the Henry's constant in [19] the corresponding concentrations of ozone in the liquid phase are 1.05×10^{-4} M and 0.58×10^{-4} M, respectively. In a few experiments, the ozonator was fed with technical grade air. The measured concentrations of oxygen in the reacting solution were very close to equilibrium (1.3×10^{-3} M for pure O_2 and 2.6×10^{-4} M for the He–O_2) and were almost unchanged by the possible presence of ozone.

Formate and formic acid were utilized as model compounds for the oxidation experiments in the reactor. These compounds have relatively simple pathways of mineralization, so that the analysis of the kinetic data is simplified. Furthermore, formic acid and formate are short chain organic molecules, which are representative of some chemical species, which are commonly formed during the oxidation of more complex organic compounds. Moreover, the rate of direct attack of ozone to these organic compounds is sufficiently low to take advantage of the synergism between ozone and photocatalysis [17].

4-Nitrophenol (4-NP) was utilized in some experiments as a model organic compound containing nitrogen. All the chemicals (Sigma–Aldrich) were of laboratory grade and were used without further purification. The aqueous solutions were prepared with de-ionized water.

The photocatalyst is commercial TiO_2 Degussa Aeroxide P25. A weighted amount of the photocatalytic powder was vigorously dispersed for 15 min in a given volume of the solution to obtain a uniform suspension. The photocatalyst concentration was $0.2\,g\,L^{-1}$ unless otherwise indicated. This value is sufficiently high to permit an almost complete absorption of the photons in the reactor.

The temperature was maintained constant at about 300 K during all the experiments. Before any experiment, the reactor was maintained without illumination for 30 min in order to permit "dark" adsorption of the chemicals and to reach steady concentrations in the suspensions.

The volume of the samples withdrawn for the chemical analysis was $3\,cm^3$. The collected samples were immediately filtered in a PTFE filter (Millipore) with $0.2\,\mu m$ pores to separate the TiO_2 powders.
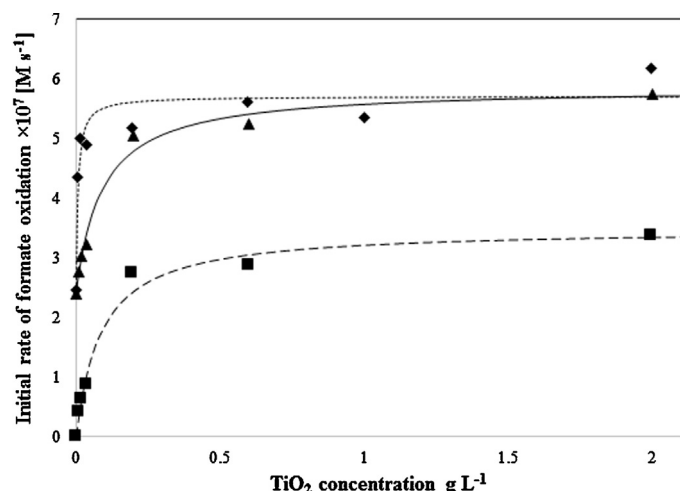
Fig. 2. Initial oxidation rate of formate vs. TiO$_2$ concentration. PC (■, dashed line), PO (♦, dotted line) and the sum of the rates in PC and in OZ (▲, continuous line). Ozone concentration in the liquid phase: 1.05×10^{-4} M, oxygen concentration $\approx 1.3 \times 10^{-3}$ M, initial concentrations of formate and bromide both equal to 0.5×10^{-3} M, pH ≈ 5.7.

The concentrations of the anionic species (bromide and bromate) were measured by an ion chromatograph system (Dionex DX 120) equipped with an Ion Pac AS14 4 mm column (250 mm long, Dionex). The eluent was an aqueous solutions of NaHCO$_3$ (8×10^{-3} M) and Na$_2$CO$_3$ (3.5×10^{-3} M) with a flow rate of 1.67×10^{-2} cm^3 s^{-1}. The 4-NP concentration was measured by means of an UV–Vis spectrophotometer (Shimadzu).

The gaseous concentration of ozone was obtained by measuring the absorbance of the gas mixture at 254 nm by a UV–Vis spectrophotometer (Shimadzu). The preliminary calibration was obtained by bubbling the O$_2$–O$_3$ mixture in KI aqueous solution and measuring the amount of iodide anion oxidized to iodate by ozone. A trap with an aqueous solution of KI abated the residual ozone leaving the reactor.

3. Results and discussion

3.1. Existence of optimal conditions for the maximization of the synergistic effect

In Fig. 2, the rates of formate oxidation in PO and PC are compared with the sum of the rates in PC and in OZ vs. the TiO$_2$ concentration. At dark, the rate of OZ is almost unaffected by the presence of TiO$_2$ and therefore the shape of the continuous curve in Fig. 2 is practically the same of the dashed one. It is apparent that the rate with the integrated process (PO) is higher than the sum of the same two uncoupled processes. This outcome clearly indicates a synergy between PC and OZ.

This synergistic effect has been observed for various organic compounds and many researchers have discussed the reasons (see e.g. [15,17,20–25]). In short, the combination of PC and OZ promotes the generation of free radicals, in particular hydroxyl radicals, which are the strongest oxidants in water [26]. A brief examination of the mechanisms, which underlie the synergy, might be useful to identify the intervening factors and to introduce a new parameter, which may affect substantially the synergy.
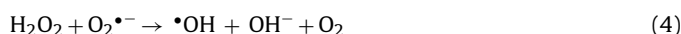
The oxidation of organic species by ozone without photocatalysis takes place in two different ways:

- direct ozonation;
- or indirectly through the hydroxyl radicals produced by ozone decomposition.

When pH is increased, the ratio of indirect oxidation to direct oxidation rises. As a result, oxidation and mineralization of recalcitrant organic compounds become faster, since hydroxyl radicals are more reactive than ozone [12].

Hydroxyl radicals are produced also in semiconductor photocatalysis:

- by the oxidation of water caused by the photogenerated holes;
- or by interface electron transfer to molecular oxygen according to the following reactions:

$$3\,O_2 + 3\,e^- \rightarrow 3\,O_2^{\bullet-} \tag{1}$$

$$2\,O_2^{\bullet-} + 2\,H^+ \rightarrow 2\,HO_2^{\bullet} \tag{2}$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{3}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^{\bullet}OH + OH^- + O_2 \tag{4}$$

Eqs. (1)–(4) have been written in a form evidencing that this mechanism requires three electrons for generating one $^{\bullet}$OH radical and it consists of four steps.

Ozone and the photocatalyst (titanium dioxide) surface interact in various ways [27–29]: (i) physical adsorption; (ii) formation of weak hydrogen bonds with the surface hydroxyl groups of the catalyst; and (iii) dissociative adsorption on the strong surface Lewis acid sites leading to O$_3$ decomposition with the formation of a free oxygen molecule and a surface oxygen atom that remains attached to the site [28].

Because of the adsorption of ozone on the photocatalyst, additional ways are viable to produce hydroxyl radicals in PO.

For instance, the adsorbed ozone may act as an electron scavenger forming an ozonide radical (O$_3^{\bullet-}$) in the adsorption layer:

$$O_3 + e^- \rightarrow O_3^{\bullet-} \tag{5}$$

Then, the ozonide radical rapidly reacts with H$^+$ to give HO$_3^{\bullet}$ (Eq. (6)), which in turn produces molecular oxygen and $^{\bullet}$OH radicals (Eq. (7)).

$$O_3^{\bullet-} + H^+ \rightarrow HO_3^{\bullet} \tag{6}$$

$$HO_3^{\bullet} \rightarrow O_2 + {}^{\bullet}OH \tag{7}$$

In this case one electron is required to produce one $^{\bullet}$OH radical in three steps.

In addition to this mechanism, it was also proposed [30] that ozone could react with O$_2^{\bullet-}$:

$$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2 \tag{8}$$

producing ozonide radicals which in turn evolve to $^{\bullet}$OH radicals according to Eqs. (6) and (7). Also in this case the production of one hydroxyl radical involves the utilization of one electron and three steps.

By comparing all the previous mechanisms, it appears that in PO the generation of hydroxyl radicals is more effective than in ozonation or in photocatalysis with oxygen. This is particularly true at low pH, where the indirect ozonation is negligible [17].

Furthermore, it must be considered that ozone is more easily adsorbed than oxygen and is a stronger oxidizing agent ($E^0 = 2.08$ V) than oxygen ($E^0 = 1.23$ V), thus ozone is a more effective electron scavenger with respect to oxygen. So, the presence of ozone reduces electron–hole recombination and, as a consequence, enhances both the rate of production of $^{\bullet}$OH radicals by water oxidation and the direct oxidation of organic compounds by the photogenerated holes.

Also hydrogen peroxide is an efficient electron acceptor which reacts with the photogenerated electrons to form hydroxyl radicals [17]. Staehelin and Hoigné [31] observed that hydrogen peroxide is produced by ozonation of waters, which contain certain organic
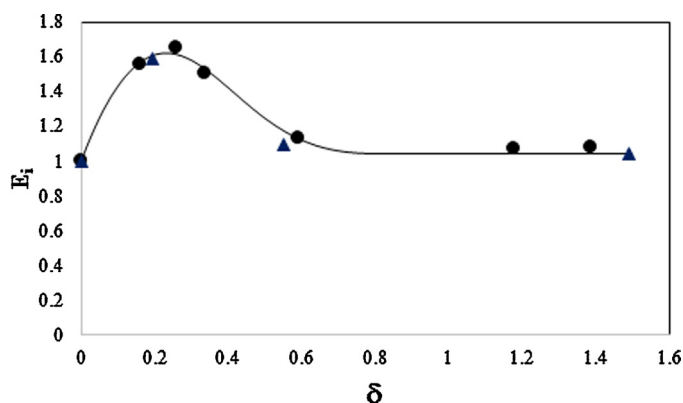
Fig. 3. Values of the intensification factor, E_i, of the integrated process vs. the ratio δ between the rate of photocatalysis and the one of ozonation. Ozone concentration in the liquid phase: 1.05×10^{-4} M (●) and 0.58×10^{-4} M (▲). Initial concentrations of formate and bromide both equal to 0.5×10^{-3} M, pH ≈ 5.7.

compounds. Therefore, as Mena et al. [17] showed for the PO of an aqueous solution of methanol, it is expected that the hole–electron recombination is reduced and the rate of formation of hydroxyl radicals is enhanced if hydrogen peroxide is produced by the ozonation of the organic compounds.

All these mechanisms explain the enhancement of the rate with PO. The "process intensification" [32], which is obtained by the integration of photocatalysis with ozonation, can be quantified by evaluating the "intensification factor", E_i, of the integrated process [33]. E_i is defined as

$$E_i = \frac{\text{oxidation rate in PO}}{\text{oxidation rate in PC} + \text{oxidation rate in OZ}}$$

The higher is the value of E_i the more important is the synergetic effect. Of course, E_i depends on the operating conditions. In fact, in Fig. 2 it is apparent that the difference between the dotted curve and the continuous one is larger at intermediate values of C_{TiO_2}, while it vanishes at low and high values of C_{TiO_2}. Actually, when a synergy holds between two processes which contribute to accomplish the same task (in this case the oxidation of organic compounds), it is expected that the extent of the synergy depends primarily on the ratio, δ, between the rates of the two processes carried out individually at the same operating conditions [33]. This aspect is generally disregarded in PO, whereas it might explain why in some cases the values of the intensification factors measured by different researchers are very dissimilar. In the present system, δ represents the ratio of the rate of PC to the one of OZ. It has been varied by conducting experiments at different concentration of photocatalyst and at two different values of ozone concentration, thus changing both the rate of photocatalysis and the rate of ozonation. The results are shown in Fig. 3.

It can be observed that, for the investigated system and at a given pH (pH ≈ 5.7), the curve is unique, thus confirming that δ is the main parameter which affects the intensification factor. In other words, the same intensification factor can be obtained for different couples of photocatalyst concentration and ozone concentration, provided that the ratio of the rates, δ, remains the same. Actually, the photocatalyst concentration and the ozone concentration influence only the rates of the individual processes, but the mechanisms, which cause the synergy, are not changed. Conversely, it is expected that if the factors influencing the mechanisms of the synergy (i.e. the type of photocatalyst, the target organic compound, and the pH) are changed, then the curve of the intensification factor vs. δ could vary.

Of course, the limits of E_i for $\delta \rightarrow 0$ (only OZ) and for $\delta \rightarrow \infty$ (only PC) are both 1. An obvious consequence is that, in whatever system, just one value of E_i greater than 1 implies the existence of an optimal value of δ that maximizes E_i.

In the investigated system, the curve in Fig. 3 shows a maximum value of the intensification factor at $\delta_{opt} \approx 0.3$. Therefore, in the case of the PO of formate with Degussa P25, a relatively low rate of photocatalysis ($\delta_{opt} \approx 0.3 < 1$) is sufficient to get the maximum synergy.

These results have important practical implications: (i) studies or applications of PO should take into account the effect of δ; (ii) the optimal value of δ should be found; and (iii) if the rate of one of the two coupled processes is changed, it is advisable to vary concurrently also the rate of the other one to continue to work with the same (maximum) degree of synergy.

3.2. Influence of pH and of some organic compounds on bromate reduction by photocatalysis

A study on the capability of PC, OZ and PO to get rid of noxious organic compounds must take into account also the possible by-production of hazardous substances, whose formation should be avoided or controlled. Bromate is the main by-product of concern when ozonation is used in presence of bromide ions. In fact, it is the only ozonation by-product which is regulated in drinking waters at a low limit of $10\,\mu g\,L^{-1}$.

In presence of ozone, bromate ions are produced by the oxidation of bromide, which is ubiquitously present in many waters, according to the equation:

$$Br^- + 3\,O_3 \rightarrow BrO_3^- + 3\,O_2 \tag{9}$$
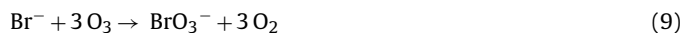
Song et al. [34] reported also other pathways in which bromate formation occurs by the action of the hydroxyl radicals produced by ozone decomposition. This latter mechanism is non-negligible only at relatively high pH values.

In a previous work [18] it was observed that as long as an oxidizable organic is present (such as formate) the formation of bromate is hindered and that, even in absence of organics, photocatalysis is able to reduce bromate back to innocuous bromide. These are the basis for the present study of the effect of pH and of the presence of organics on the reduction of bromate.

Firstly, it has been established (see Figs. S1–S3 of the Supplementary material) that, without TiO_2 and without organic compounds, bromate ions are stable in solution regardless of the presence of oxygen, ozone and irradiation with UVA.

At pH ≈ 5.7, which is the value obtained with no pH adjustment, photocatalysis in aqueous TiO_2 suspension causes the reduction of bromate to bromide even in the presence of oxygen as shown in Fig. 4. Without illumination the reduction of bromate does not take place, in fact it begins only when the lamp is switched on at $t = 0$. Besides, the sum of bromide and bromate remains constant, so the concentration of other ions containing Br, such as hypobromite, can be considered negligible.

On the other hand, when the pH was initially adjusted at 9, by adding NaOH, bromate reduction does not takes place in presence of oxygen (see Fig. S4 of the Supplementary material). This result can be explained taking into account that the isoelectric point of TiO_2 P25 is 6.2 [35]. Therefore, when the pH is higher than 6.2, the surface of TiO_2 is negatively charged and the hydroxyl groups on the TiO_2 surface are mainly deprotonated according to the following equation:

$$Ti-OH + OH^- \leftrightarrows Ti-O^- + H_2O \tag{10}$$

In these conditions, the electrostatic interactions between BrO_3^- and the TiO_2 surface are weak, the adsorption of BrO_3^- is low and oxygen reduction takes place in place of bromate reduction. Furthermore, the redox potential of oxygen (1.23 V vs. NHE) is very similar to the one of bromate (1.15 V), so kinetic factors
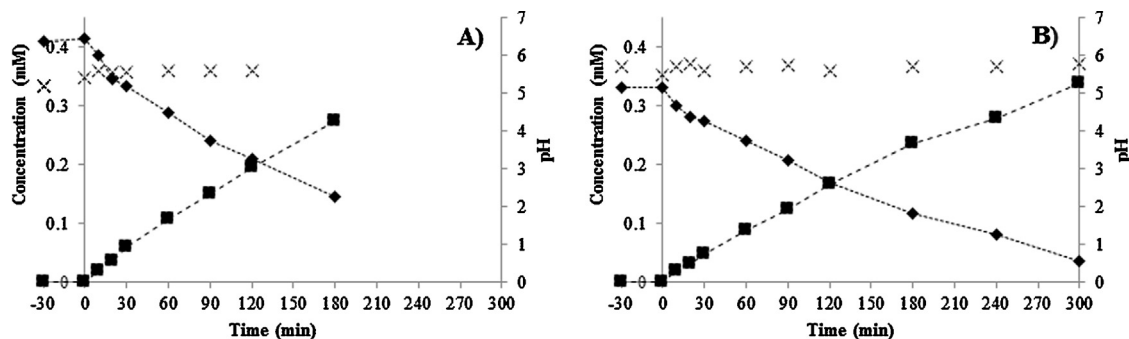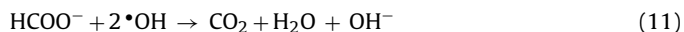
Fig. 4. Bromate (♦), bromide (■) concentrations and pH values (×) vs. irradiation time in a PC experiment. (A) Solution saturated with pure oxygen (oxygen concentration $\approx 1.3 \times 10^{-3}$ M) and (B) without oxygen (N_2 bubbled).

may easily change the preferential reduction. A similar effect of the pH on the adsorption and the photocatalytic reaction has been reported for Ag deposition [36], for photo-oxidation of ferulic acid [37] and degradation of formic acid [38] on TiO_2 photocatalyst. The second order kinetic with respect to the proton concentration for the reactivity of BrO_3^- as an oxidizing agent [39] represents another reason of the low probability of bromate reduction taking place at high values of pH.

On the contrary, pH values lower than the zero point charge of the photocatalyst improve bromate reduction because of the enhanced interaction between BrO_3^- with the positively charged surface of TiO_2. A similar effect has been observed also for activated carbon [39] and for pseudo-boehmite modified TiO_2 [40].

As shown in the previous section PC, OZ and PO are effective methods, in particular PO, to degrade organic compounds. Therefore, it is worthwhile to investigate the possible effect of the presence of organic compounds on the reduction of bromate by PC.

The results obtained with formate in solution are shown in Fig. 5. Bromate reduction to bromide appears to be slow and, after the complete degradation of formate, bromate concentration is almost stable. This outcome can be ascribed again to the inhibiting action of high pH, which from the initial value of pH = 6 rapidly reaches a plateau at pH = 9. The raise of the pH is a consequence of formate degradation, which produces hydroxyl ions according to Eq. (11).

$$HCOO^- + 2\,{}^{\bullet}OH \rightarrow CO_2 + H_2O + OH^- \tag{11}$$

In order to prove that pH is really a key parameter for the photocatalytic bromate reduction, PC and PO were carried out in similar conditions, but at a lower pH. To this end, formate was substituted with formic acid in order to maintain a lower pH. The results are shown in Fig. 6.

Both PC (Fig. 6A) and PO (Fig. 6B) were able to degrade formic acid and to reduce bromate to bromide. By considering that ozone has a strong tendency to oxidize bromide to bromate, the
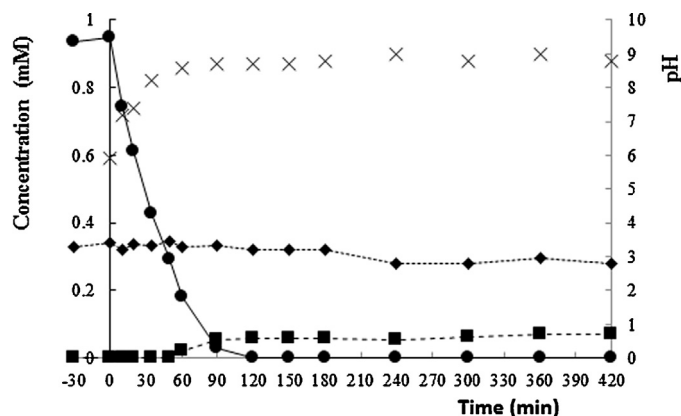

Fig. 5. Bromate (♦), bromide (■), formate (●) concentrations and pH values (×) in a PC experiment with pure oxygen (oxygen concentration $\approx 1.3 \times 10^{-3}$ M).

reduction of bromate obtained in PO is rather surprising and it is a consequence of the coupling with photocatalysis. In fact, bromate reduction does not take place in ozonation without photocatalysis regardless of the pH and the presence of organic compounds (see Fig. S5 of the Supplementary material). In PO the reduction takes place only as long as formic acid is present in the reacting mixture. After the disappearance of formic acid, bromide is oxidized again to bromate, as it usually happens when ozone is present. It is likely that the organic compound (in this case formic acid) acts as a hole trap, reducing electron–hole recombination and making electrons more available for bromate reduction.

To confirm this hypothesis, the reduction of bromate was studied also in the presence of methanol, which is characterized by a relatively high oxidation potential.

Fig. 7 shows the results of a photocatalytic experiment carried out in the presence of oxygen, bromate and methanol (1×10^{-3} M).
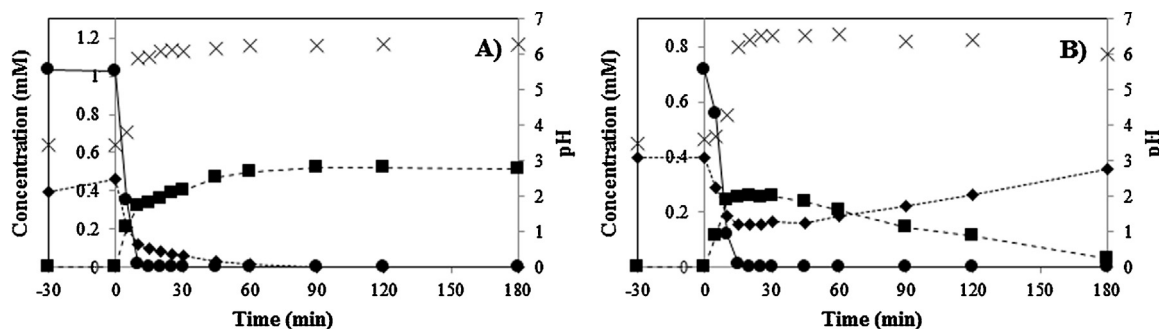

Fig. 6. Bromate (♦), bromide (■), formic acid (●) concentrations and pH values (×). (A) PC (oxygen concentration $\approx 1.3 \times 10^{-3}$ M) and (B) PO (ozone concentration $\approx 0.58 \times 10^{-4}$ M).
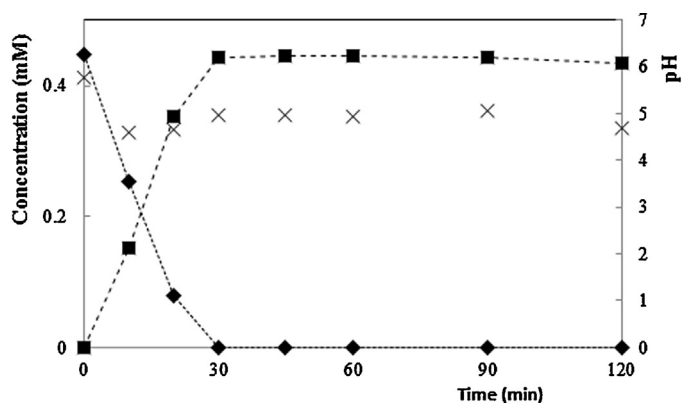
Fig. 7. Bromate (♦), bromide (■) concentrations and pH values (×). PC with pure oxygen (oxygen concentration $\approx 1.3 \times 10^{-3}$ M) and methanol (1×10^{-3} M).

Fig. 9. Bromate (♦), bromide (■), nitrate (▲) concentrations and pH values (×). OZ experiment with air fed to the ozonator.

Remarkably, the initial rate of bromate reduction in the presence of methanol (rate = 3.08×10^{-7} M s^{-1}) is higher than the one (see data in Fig. 4A) obtained without methanol (rate = 6.11×10^{-8} M s^{-1}). The difference between the rates of bromate reduction indicates that the oxidation potential of the organic compound, i.e. its capability to efficiently act as hole scavenger, is an important factor for bromate reduction.

Bromate reduction was then tested in presence of 4-NP as a model organic compound containing nitrogen atoms. Fig. 8 shows the results of a PO experiment.

It is observed that in PO at low pH, similarly to what happens with formic acid, the reduction of bromate to bromide takes place as long as 4-NP is present in the solution, but thereafter the formed bromide is again oxidized to bromate. PC also is able to reduce bromate ions to bromide ions, which, unlike in PO, remain stable after the organic compound has disappeared (see Fig. S6 of the Supplementary material).

It must be pointed out that in the oxidation of formic acid by OZ or PO it is sufficient to take into account only bromate and bromide ions to close the Br balance, however it is not so in the oxidation of 4-NP. In fact, the sum of the bromate concentration plus the bromide concentration is continuously decreasing during the runs with 4-NP, and the Br balance remains unsatisfied even taking account of hypobromite ions, whose concentration is low.

The analysis of this phenomenon must take into account that the solution contains the nitrates produced by 4-NP oxidation and the pH is quite acidic. In these conditions, nitrate ions react in the
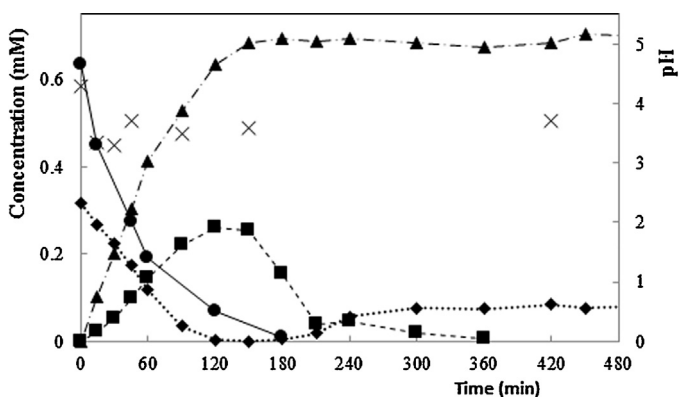
solution with bromide ions [41] to give bromine and nitrous acid according to the following reaction:

$$NO_3^- + 2 Br^- + 3H^+ \leftrightarrows Br_2 + HNO_2 + H_2O \tag{12}$$
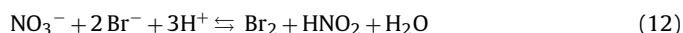
It is worth noticing that the standard redox potential (vs. NHE) of the couples Br_2/Br^- (1.087 V) and NO_3^-/NO_2^- (0.934 V) are so similar that in conditions different from the standard ones it is possible that the reaction evolves towards the Br_2 formation.

The produced bromine is stripped by the gaseous stream flowing through the suspension. Furthermore, nitrite ions can be easily re-oxidized to nitrate and only traces of nitrite can be present and detected by ion chromatography. In these conditions, the production of bromine according to Eq. (12) continues, since an equilibrium is not reached, and the oxidation of bromide through this pathway can be significant.

The presence of bromine in the gaseous stream was verified by passing this stream through the distilled water in a flask immersed in an ice cold trap. Few drops of potassium iodide were added to react with bromine and produce bromide and iodine. Then iodine was detected with some drops of starch solution, which produced the characteristic blue complex.

It is clear that the formation of nitrates and the relatively low value of the pH are the prerequisites for the undesired production of bromine from bromide.

Fig. 9 shows that, if air is fed to the ozonator, nitrates are produced also without 4-NP. In this ozonation run, nitrates were produced, the pH rapidly fell well below 7, the concentration of bromide decreased and the formation of bromate ions was very low. The presence of nitrates can be explained with the mechanism proposed by Kogelschatz et al. [42]. Inside the corona-discharge ozonator reactive oxygen and nitrogen atoms as well as excited molecules are produced within several nanoseconds. These species can react in few microseconds to give NO, NO_2, NO_3, N_2O, N_2O_5 and O_3. Among them N_2O_5 and N_2O are the most abundant products. While the reactivity of N_2O is of minor importance, N_2O_5 can react with water in the gas phase and in the reactor to give nitric acid [43]. The increase of the nitrate concentration and the decrease of the pH (see Fig. 9) are thus justified. In such acidic conditions, nitrates react with bromide ions to give bromine according to Eq. (12). Bromine was stripped from water by the gaseous stream and after 120 min the transformation of bromide was almost complete, so that the concentration of bromide in the solution became negligible. On the contrary, in an ozonation experiment (see Fig. S7 of the Supplementary material) at higher pH (pH $\approx$ 7) no formation of bromine was observed in presence of nitrates (1.2 mM). Therefore, in the case of ozonation in waters containing bromide it is advisable to avoid the utilization of air if the pH is low.

Fig. 8. Bromate (♦), bromide (■), 4-NP (●), nitrate (▲) concentrations and pH values (×). PO with ozone concentration in the liquid phase $\approx 1.05 \times 10^{-4}$ M, oxygen concentration $\approx 1.3 \times 10^{-3}$ M.
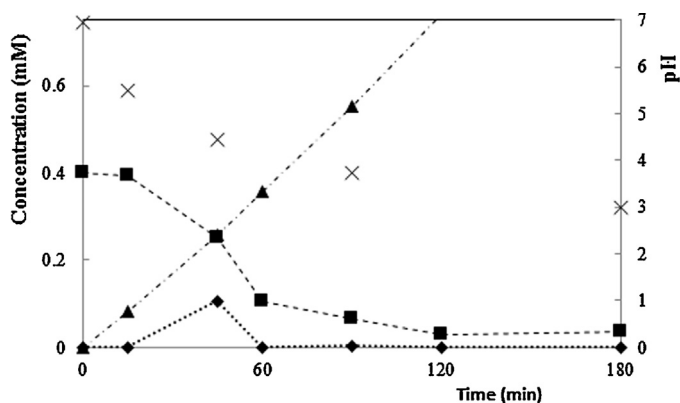
4. Conclusions

When photocatalysis is coupled to ozonation two important benefits are obtained: the enhancement of the rate of oxidation and the possibility to control the buildup of bromate, an undesired by-product of concern. Therefore, photocatalytic ozonation can be considered a really interesting candidate for different practical applications, such as aquaculture and waste and drinking water treatment.

In the present work, it is demonstrated that the synergy that occurs in this integrated process depends on δ, the ratio of the rate of photocatalysis to the one of ozonation. In the investigated system, the highest synergy is obtained at $\delta \approx 0.3$, that is when the rate of photocatalysis is only a relatively small fraction of the one of ozonation.

Besides, an effective control of the bromate buildup can be obtained by photocatalysis. In fact photocatalysis, even if it is classified as an "Advanced Oxidation Technology", does not oxidize innocuous bromide into bromate. Therefore, it can be safely used to complete the mineralization of organic compounds, after a first step of oxidation with PO. In this first step the presence of oxidizable organic compounds hinders the formation of bromate. Moreover, in the possibility that bromate ions are produced, photocatalysis is able to reduce them to innocuous bromide if the pH is not too high. The reduction of bromate by photocatalysis takes place also in presence of ozonation if organic compounds are present. Finally, it has been observed that when nitrogen is introduced in the system through organic compounds containing nitrogen atoms or through the air fed to the ozonator, acidic conditions should be avoided since nitrates are produced and react with bromide to form bromine, another undesired by-product.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2014.10.081.

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